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㉒ **Breathable films prepared from melt embossed polyolefin/filler precursor films.**

㉓ A breathable polyolefin film is prepared by melt embossing a highly filler polyolefin film to impose a pattern of different film thickness therein and by stretching the melt embossed film to impart greater permeability in the areas of reduced thickness in comparison to the areas of greater thickness.

EP 0 283 200 A2

BREATHABLE FILMS PREPARED FROM MELT EMBOSSED
POLYOLEFIN/FILLER PRECURSOR FILMS

Famer

Field of the Invention

The invention relates to Breathable polymer films --
polymer films which are gas/vapor permeable and liquid
impermeable -- prepared from highly filled polyolefin
5 film.

Related Art

It is known to prepare porous polyolefin films by
stretching a precursor film filled with calcium carbonate.
"Breathable" films which are gas/vapor permeable and
10 liquid impermeable have been described in U.S. Patent No.
4,472,328, assigned to Mitsubishi Chemical Industries,
Ltd. The Mitsubishi patent describes a breathable
polyolefin film prepared from a polyolefin/filler
composition having from 20 percent to 80 percent by weight
15 of a filler such as a surface treated calcium carbonate.
A liquid or waxy hydrocarbon polymer elastomer such as a
hydroxy-terminated liquid polybutadiene was found to
produce a precursor film that could be monoaxially or
biaxially stretched to make a film breathable. The
20 breathable film described by Mitsubishi is also described
in Great Britain Patent No. 2,115,702, assigned to Kao
Corporation. The Kao patent further describes a
disposable diaper prepared with a breathable film as
disclosed by the Mitsubishi patent. The breathable film
25 is used as a backing for the diaper to contain liquid.

U.S. Patent No. 4,350,655, assigned to Biax Fiber
Film, describes a porous polyolefin film containing at
least 50 percent by weight of a coated inorganic filler.
The precursor film is formed without the addition of an
30 elastomer by employing an inorganic filler surface coated
with a fatty acid ester of only silicon or titanium. The
precursor film is then rolled between horizontally grooved
rollers. Cold stretching of the precursor film at a

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temperature below 70°C produces a porous film. Some of the resulting films were stated to be both vapor and liquid permeable, however, at least one film (Example 3) was stated to be permeable to air.

EP-A-232 060 of earlier priority date and to be considered under Article 54(3)EPC describes the production of a gas-permeable porous film of LLDPE produced by mixing the LLDPE and a filler, extruding a film, embossing and stretching the film. The film so possesses a rugged pattern on the surface. The pattern is produced by an embossing roller and may be applied before and/or after stretching of the film. The pattern may be e.g. a satin finish or in the form of lines. US-A-4,921,653 equivalent to the above defines the rugged pattern as having peaks and valleys with a depth therebetween of from 2 μ m to 3 mm. EP-A-232 060 does not disclose the specific nature of the LLDPE other than the melt index.

The present invention provides a method of making a breathable film comprising the steps of :

- mixing a linear low density polyethylene copolymer produced by polymerising ethylene with a C₄-10 alpha olefin with a filler,
- extruding a precursor film from the copolymer /filler mixture,
- melt embossing the film to impose therein a pattern of areas of different film thicknesses, and
- stretching the film to impart greater vapor permeability in areas of reduced thickness in comparison to areas of greater thickness.

The film may be produced by tubular extrusion and embossed thereafter. Preferably a precursor film is cast extruded and embossed prior to stretching.

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The invention is inclusive of breathable film obtainable by the method described above characterised by a pattern of areas of different film thicknesses with greater vapor permeability in areas of reduced thicknesses in comparison to areas of greater thickness and an overall water vapor transmission rate in excess of 5,800 g/m²/day.

temperature below 70°C produces a porous film. Some of the resulting films were stated to be both vapor and liquid permeable, however, at least one film (Example 3) was stated to be permeable to air.

5 SUMMARY OF THE INVENTION

The present invention relates to breathable films produced by stretching of a precursor film prepared from a polyolefin/filler composition. It has been discovered that the permeability and strength, especially tear
10 strength, of the breathable films are improved by melt embossing the precursor film with a patterned melt embossing roller and stretching the film to impart a pattern of different film thicknesses having greater permeability within the areas of reduced thickness in
15 comparison to the areas of greater thickness. Cast extrusion of the precursor film onto the embossing roller followed by stretching in the transverse direction is preferred.]

20 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

Film Forming Compositions

Breathable films of the present invention are produced from a precursor film that is prepared from a
25 polymer composition that comprises at least a polyolefin component and a filler. The polyolefin component may be any polyolefin which is suitable for film production, such as polypropylene, copolymers of propylene, homopolymers and copolymers of ethylene or blends thereof. A preferred
30 polyolefin is a copolymer of polypropylene and low density polyethylene, particularly preferred is linear low density polyethylene.

Linear low density polyethylene (LLDPE) ^{as used in the present invention} is produced by copolymerizing ethylene with a C₄ to C₁₀ alpha-olefin.
35 Generally the preferred alpha-olefins include those selected from the group comprising butene-1, pentene-1, hexene-1, 4 methylpentene-1, heptene-1, and octene. The

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comonomers are present in amounts up to 20 wt. %, normally between 3 and 14 wt. %. The polymerization is conducted at low pressure using a chromium catalyst or Ziegler catalyst and may be carried out in the gas phase. The LLDPE produced by such methods have a density between 0.900 and 0.935 g/cm³ and a melt index (MI) between 0.1 and 5.0 grams per 10 minutes. Manufacturing processes for production of LLDPE are known, such as disclosed in U.S. Patent Nos. 4,076,698 and 4,205,021. LLDPE is preferred as the polyolefin component for use in this invention because of its high tear strength, ease of compounding, and low cost.

Fillers useful in this invention may be any inorganic or organic material having a low affinity for and a significantly lower elasticity than the polyolefin component. Preferably the filler should be a rigid material having a non-smooth hydrophobic surface, or a material which is treated to render its surface hydrophobic. The preferred mean average particle size of the filler is between about 3 to 5 ^{microns} ~~microns~~ for films having a thickness of between ^{0.1-1.5 mm} (4-6 mil) prior to stretching. Examples of the inorganic fillers include calcium carbonate, talc, clay, kaolin, silica, diatomaceous earth, magnesium carbonate, barium carbonate, magnesium sulfate, barium sulfate, calcium sulfate, aluminum hydroxide, zinc oxide, magnesium hydroxide, calcium oxide, magnesium oxide, titanium oxide, alumina, mica, glass powder, zeolite, silica clay, etc. Calcium carbonate is particularly preferred for low cost, whiteness, inertness, and availability. The inorganic fillers such as calcium carbonate are preferably surface treated to be hydrophobic so that the filler can repel water to reduce agglomeration of the filler. Also, the surface coating should improve binding of the filler to the polymer while allowing the filler to be pulled away from the polyolefin under stress. A preferred coating is calcium stearate which is FDA approved and readily available. Organic fillers such as wood powder, pulp powder, and other cellulose type powders

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may be used. Polymer powders such as Teflon[®] powder and Kevlar[®] powder can also be used.

The amount of filler added to the polyolefin depends on the desired properties of the breathable film including
5 tear strength, water vapor transmission rate, and stretchability. However, it is believed that a breathable film cannot be produced as is taught herein with an amount of filler less than about 15 percent by volume of the polyolefin/filler composition (e.g. LLDPE/CaCO₃ having
10 less than about 38 percent by weight CaCO₃). The minimum amount of filler is needed to insure the interconnection within the film of voids created at the situs of the filler particularly by the stretching operation to be subsequently performed on the precursor film. Further, it
15 is believed that useful films could not be made with an amount of the filler in excess of about 35 percent by volume of the polyolefin/filler composition (e.g. LLDPE/CaCO₃ having greater than about 65 percent by weight CaCO₃). Higher amounts of filler may cause difficulty in
20 compounding and significant losses in strength of the final breathable film.

Polyolefin/filler compositions usable in this invention may be compounded in several different ways. The components may be brought into intimate contact by,
25 for example, dry blending these materials and then passing the overall composition through a compounding extruder. Alternatively, the polyolefin and filler components may be fed directly to a mixing device such as a compounding extruder, high shear continuous mixer, two roll mill or an
30 internal mixer such as a Banbury mixer. Overall, the objective is to obtain a uniform dispersion of the filler in the polymer without agglomeration, and this is readily achieved by inducing sufficient shear and heat to cause the polyolefin component to melt. However, time and
35 temperature of mixing should be controlled as is normally done to avoid molecular weight degradation. Compounding of LLDPE and calcium carbonate that is surface treated

with calcium stearate has been improved by vacuum drying the mixture within the extruder.

The tear strength and softness of a film prepared from the polyolefin/filler composition may be improved by addition of small amounts of an olefinic elastomer.

Film Extrusion and Melt Embossing

The film forming composition may be manufactured into a precursor film by conventional tubular extrusion (blown bubble process) or by cast extrusion. Film formation by cast extrusion is preferred because the cast film can be immediately melt embossed as described below.

In the cast extrusion process, the molten resin is extruded from an elongate die in the form of a web. The web is pulled over at least one patterned embossing roller to chill and solidify the film with an embossed pattern for reasons discussed further below. The precursor film is preferably produced to a gauge of ¹⁰¹⁴/₁₅₂ mm (4 to 6 mils), which allows for further stretching as described below. The extrusion temperatures, die temperatures, and embossing roll temperatures will depend on the composition employed, but generally will be in the following ranges for compositions of the present invention prepared by cast extrusion:

Melt Temperature ($^{\circ}\text{F}$) $\frac{177-232}{3-4}^{\circ}\text{C}$ (350-450 $^{\circ}\text{F}$)
Die Temperature ($^{\circ}\text{F}$) $\frac{177-232}{3-4}^{\circ}\text{C}$ (350-450 $^{\circ}\text{F}$)
Embossing Roll Temperature ($^{\circ}\text{F}$) $\frac{215-240}{1}^{\circ}\text{C}$ (70-130 $^{\circ}\text{F}$)

Film formation by tubular extrusion produces balanced films having increased film strength in both the machine and cross-machine direction. In the tubular blown film process, the film forming composition is first melted and then extruded through an annular die. The die should preferably have a die gap suitable for extruding LLDPE resin which normally is greater than about 0.5 mm and preferably greater than 0.75 mm. The film forming composition is extruded at a melt temperature between about 150 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$, preferably between 190 $^{\circ}\text{C}$ and 240 $^{\circ}\text{C}$. The molten composition is preferably extruded in an upward

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vertical direction in the form of either a bubble or a tube, although it also can be extruded either downwardly or horizontally. The tubular extrudate is expanded to the desired dimensions and then cooled by one of several
5 conventional techniques which are well known in the art, e.g., forced air, mandrel, and water quench. The tubular film, or bubble, is then flattened by passing the film through a collapsing frame and a set of nip rolls. The nip rolls are driven, thereby providing a means of drawing
10 the tubular film or bubble away from the annular die.

A positive pressure of a gas, such as air or nitrogen, is maintained inside the tubular bubble. As is known in the operation of conventional blown film processes, the presence of the gas is controlled to impart
15 a desired dimensional orientation to the film tube or bubble. The degree of tubular bubble expansion may be measured as the ratio of the expanded bubble circumference to the circumference of the die annulus. This ratio is generally in the range of 1 : 1 to 6 : 1 and for a
20 precursor breathable film is preferably from 2 : 1 to 4 : 1.

Embossing is typically used on the surface of polyolefin films to reduce gloss. Embossing can be imposed on the precursor film surface at the time of the
25 film fabrication for cast extrusion, or at a subsequent time for cast or tubular extrusion by procedures well known in the art. For the present invention, embossing imposes a pattern of different film thicknesses within the precursor film, and can be conducted with any micro/macro
30 pattern, e.g. cross-hatching, dots, lines, circles, diamonds, hexagons etc. The pattern can be either in line and/or off line and the rolls can be engraved with either pin up and/or pin down type configurations.

Stretching and Heat Setting

35 Final preparation of a breathable film is achieved by stretching the precursor film to form interconnected voids. Stretching or "Orientation" of the film may be carried out monoaxially in the machine direction (MD) or

the transverse direction (TD) or in both directions (biaxially) either simultaneously or sequentially using conventional equipment and processes following cooling of the precursor film.

5 Blown films are preferably stretched in the machine direction or in both directions whereas cast films are preferably stretched in the transverse direction. For orientation in the MD, the precursor film is passed around two rollers driven at different surface speeds and finally
10 to a take up roller. The second driven roller which is closest to the take up roll is driven faster than the first driven roller. As a consequence the film is stretched between the driven rollers.

15 Film orientation may also be carried out in a tentering device with or without MD orientation to impart TD orientation to the film. The film is gripped by the edges for processing through the tentering device.

20 Stretching of melt embossed precursor films with a tentering device at a film speed of about 60 meters per minute produced breathable films having the desired water vapor permeability. The resulting films had greater permeability in the areas of reduced thickness in comparison to the areas of greater thickness.

25 Although not thoroughly investigated, controlling of the strain on the film during stretching is believed to be important to controlling the permeability. For stretching in the transverse direction, strain is controlled for a given stretch ratio by adjusting the film speed and the stretching distance. The stretching distance is measured,
30 between the point where the film starts to increase in width to the closest point where the film is fully stretched. For stretching in the machine direction, strain is controlled for a given stretch ratio by controlling film speed and the gap between the first and
35 second driven rollers.

A range of stretching ratios from 1:2 to 1:5 prove satisfactory for MD stretching with a ratio of 1:4 being preferred. A range of stretching ratios of 1:2 to 1:5

prove satisfactory for TD stretching with a ratio of 1:4 being preferred.

5 The water vapor permeability of the embossed film following stretching, as measured by the final WVTR of the film, was found to be inversely related to the stretching temperature. Stretching at a temperature of about 45°C produced a film having a slightly higher WVTR than stretching at temperatures of about 60°C.

10 The stretched film can be heat set to stabilize the film for any subsequent processing at temperatures above the stretching temperature. The film can be heat set at any temperature above the stretching temperature and below the softening temperature to add stability. However, higher temperatures cause stiffness and some reduction in WVTR. Heat setting at about 80°C produced a softer film
15 with substantially higher WVTR in comparison to heat setting at about 95°C.

It is preferred that tension be maintained on the film during the heat setting and cooling to minimize shrinkback. Upon cooling to ambient temperature (i.e.,
20 room temperature) or near ambient, the holding force may be released. The film may contract somewhat (snapback) in the TD but will retain a substantial portion of its stretched dimension.

25 Heat setting can be accomplished by maintaining the film under tension in the stretched condition at the heat setting temperature for about 1 - 2 minutes. Preferably, however, the heat setting and cooling is carried out while permitting the film to contract slightly, but still under stress. The controlled shrinkback of from 5 to 30%,
30 preferably between 15 and 25%, of the maximum stretched width has given particularly good results in eliminating storage shrinkage.

EXAMPLES

35 The following examples, which illustrate melt embossed breathable films prepared in accordance with the present invention, are not intended to limit the invention to the specific compositions. Other compounds such as

elastomers, stabilizers against heat or ultraviolet rays, pigments, antistatic agents, etc. may be added to the compositions in the conventional manner. Variations in composition and manufacturing techniques will be readily apparent to persons skilled in the art of manufacturing polyolefin films and are within the scope of this invention. In the examples which follow water vapor transmission rates (WVTR) were measured in accordance with ASTM F372-73 using a PermTRAN W1 analyzer manufactured by Modern Controls International Inc.

Example 1 (COMPARISON)

A linear low density polyethylene which consisted of a copolymer of ethylene and hexene-1 was compounded with an equal weight of a surface treated calcium carbonate. The calcium carbonate was surface treated with calcium stearate to render the surface of the particles hydrophobic. The resulting formulation was cast extruded into a precursor film having a thickness of approximately (4 to 6 mil).

The resulting precursor film was cooled and then subjected to tentering stress in the transverse direction with a stretch ratio of 4 to 1 and a film speed of about 60 meters per minute. Stretching was performed in a tentering frame with heat applied only to the final zone of the tentering frame. The temperature of the film in the final zone was maintained at about 93°C. As a result of convection within the tentering frame, stretching of the film occurred at approximately 60°C. The film became white and breathable when stretched and retained those properties following the heat setting treatment. The final breathable film had a water vapor transmission rate of up to 5800 grams per square meter per day at 38°C.

Example 2

The LLDPE/calcium carbonate composition of Example 1 was cast extruded under the same conditions as Example 1. The precursor film was passed between a smooth roller and a diamond patterned embossing roller. The resulting film had a thickness of approximately (4 to 6 mil) and a diamond

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pattern on one side. The film became whiter when stretched at the temperature and conditions stated for Example 1. Heat setting was also conducted as described for Example 1. This film had a WTVR value of 8,100 grams per square meter per day. Stretching caused greater permeability in the thin portions of the film created by the embossing roll in comparison to the thick area which retained greater strength. The final film had a drapy and softer film structure and a higher tear strength than the film of Example 1.

Example 3

The LLDPE/filler composition of Example 1 was extruded and melt embossed under the same conditions of Example 2. The precursor film was then stretched with the tentering device of Example 2. The temperature of the film in the heat setting zone was maintained at about 78°C and stretching occurred at about 35°C. The final film had a WTVR value of 10,300 grams per square meter per day.

Example 4

A breathable film was prepared under the same conditions of Example 3 except that the stretching temperature was adjusted to 70°C. The final film had a WTVR value of 10,000 grams per square meter per day.

Example 5

A breathable film was prepared under the same conditions of Example 3 except that the stretching temperature was adjusted to 93°C. The final film had a WTVR value of 9,900 grams per square meter per day.

The following table presents a comparison of the variables in Examples 1-5.

	Stretch Temp., °C	Heat Set Temp., °C	WTVR g/m ² /day
Example 1 (Comparison)	60	93	5,800
Example 2	60	93	8,100
35 Example 3	35	78	10,300
Example 4	70	78	10,000
Example 5	93	78	9,900

USES

The breathable films of the present invention can replace currently available breathable films in such applications as diaper back sheets and light weight camping and backpacking equipment. Breathable films are expected to have a wide variety of applications in the fields of medical and surgical supplies, apparel and household furnishings, tape and packaging, and filtration membranes. For example, breathable films can be used to replace porous films in applications such as burn dressings, sterile packaging, rain coats, shoe linings, nonfogging packaging film, bacteria filters, water purification filters, and wind insulation of houses and buildings.

CLAIMS

1. Method of making a breathable film comprising the steps of :
mixing a linear low density polyethylene copolymer produced by polymerising ethylene with a C₄-10 alpha olefin with a filler,
extruding a precursor film from the copolymer/filler mixture,
melt embossing the film to impose therein a pattern of areas of different film thicknesses, and
stretching the film to impart greater vapor permeability in areas of reduced thickness in comparison to areas of greater thickness.
2. Method according to claim 1 wherein the filler is calcium carbonate treated with calcium stearate.
3. Method according to claim 1 or claim 2 wherein the copolymer/filler mixture contains from 15 to 35 vol % filler.
4. Method according to any preceding claim wherein said alpha-olefin is selected from butene-1, pentene-1, 4-methylpentene-1, heptene-1 and octene.
5. Method according to any of claims 1 to 3 wherein said alpha-olefin is hexene-1.
6. Method according to any preceding claim wherein said alpha-olefin is present in amount from 3 to 14 wt %.

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7. Method according to any preceding claim wherein said LLDPE copolymer has a density from 0.900 to 0.935 g/cm³.
8. Method according to any preceding claim wherein the unstretched film has a thickness from 102 to 152 μ m (4 to 6 mil).

9. Method according to any preceding claim wherein the film is produced by tubular extrusion and embossed thereafter.
10. Method according to any of claims 1 to 8 wherein a precursor film is cast extruded and embossed prior to stretching.
11. Method according to claim 10 wherein the precursor film is extruded at a melt and/or die temperature from 177 to 232°C (350 to 450°F.)
12. Method according to claim 10 or claim 11 comprising the step of heat setting the stretched film at a temperature above the stretching temperature and below the softening temperature of the stretched film.
13. Method according to claim 12 wherein the stretched film is heat set at a temperature from 60 to 95°C.
14. Breathable film obtainable by the method of claim 1 characterised by a pattern of areas of different film thicknesses with greater vapor permeability in areas of reduced thickness in comparison to areas of greater thickness and an overall water vapor transmission rate in excess of 5,800 g/m²/day.
15. Breathable film according to claim 14 having a said pattern of areas in the form of circles or hexagons.
16. Breathable film according to claim 14 having a said pattern of areas in the form of diamonds.

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ABSTRACT

BREATHABLE FILMS PREPARED FROM MELT EMBOSSED
POLYOLEFIN/FILLER PRECURSOR FILMS

A breathable polyolefin film is prepared by melt
embossing a highly filled polyolefin film to impose a
pattern of different film thickness therein and by
stretching the melt embossed film to impart greater
5 permeability in the areas of reduced thickness in
comparison to the areas of greater thickness.

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temperature below 70°C produces a porous film. Some of the resulting films were stated to be both vapor and liquid permeable, however, at least one film (Example 3) was stated to be permeable to air.

5 SUMMARY OF THE INVENTION

The present invention relates to breathable films produced by stretching of a precursor film prepared from a polyolefin/filler composition. It has been discovered that the permeability and strength, especially tear strength, of the breathable films are improved by melt embossing the precursor film with a patterned melt embossing roller and stretching the film to impart a pattern of different film thicknesses having greater permeability within the areas of reduced thickness in comparison to the areas of greater thickness. Cast extrusion of the precursor film onto the embossing roller followed by stretching in the transverse direction is preferred.

20 DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

Film Forming Compositions

Breathable films of the present invention are produced from a precursor film that is prepared from a polymer composition that comprises at least a polyolefin component and a filler. The polyolefin component may be any polyolefin which is suitable for film production, such as polypropylene, copolymers of propylene, homopolymers and copolymers of ethylene or blends thereof. A preferred polyolefin is a copolymer of polypropylene and low density polyethylene, particularly preferred is linear low density polyethylene.

Linear low density polyethylene (LLDPE) is produced by copolymerizing ethylene with a C₄ to C₁₀ alpha-olefin. Generally the preferred alpha-olefins include those selected from the group comprising butene-1, pentene-1, hexene-1, 4 methylpentene-1, heptene-1, and octene. The

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comonomers are present in amounts up to 20 wt. %, normally between 3 and 14 wt. %. The polymerization is conducted at low pressure using a chromium catalyst or Ziegler catalyst and may be carried out in the gas phase. The LLDPE produced by such methods have a density between 0.900 and 0.935 g/cm³ and a melt index (MI) between 0.1 and 5.0 grams per 10 minutes. Manufacturing processes for production of LLDPE are known, such as disclosed in U.S. Patent Nos. 4,076,698 and 4,205,021. LLDPE is preferred as the polyolefin component for use in this invention because of its high tear strength, ease of compounding, and low cost.

Fillers useful in this invention may be any inorganic or organic material having a low affinity for and a significantly lower elasticity than the polyolefin component. Preferably the filler should be a rigid material having a non-smooth hydrophobic surface, or a material which is treated to render its surface hydrophobic. The preferred mean average particle size of the filler is between about 3 to 5 microns for films having a thickness of between 4-6 mil prior to stretching. Examples of the inorganic fillers include calcium carbonate, talc, clay, kaolin, silica, diatomaceous earth, magnesium carbonate, barium carbonate, magnesium sulfate, barium sulfate, calcium sulfate, aluminum hydroxide, zinc oxide, magnesium hydroxide, calcium oxide, magnesium oxide, titanium oxide, alumina, mica, glass powder, zeolite, silica clay, etc. Calcium carbonate is particularly preferred for low cost, whiteness, inertness, and availability. The inorganic fillers such as calcium carbonate are preferably surface treated to be hydrophobic so that the filler can repel water to reduce agglomeration of the filler. Also, the surface coating should improve binding of the filler to the polymer while allowing the filler to be pulled away from the polyolefin under stress. A preferred coating is calcium stearate which is FDA approved and readily available. Organic fillers such as wood powder, pulp powder, and other cellulose type powders

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with calcium stearate has been improved by vacuum drying the mixture within the extruder.

The tear strength and softness of a film prepared from the polyolefin/filler composition may be improved by addition of small amounts of an olefinic elastomer.

Film Extrusion and Melt Embossing

The film forming composition may be manufactured into a precursor film by conventional tubular extrusion (blown bubble process) or by cast extrusion. Film formation by cast extrusion is preferred because the cast film can be immediately melt embossed as described below.

In the cast extrusion process, the molten resin is extruded from an elongate die in the form of a web. The web is pulled over at least one patterned embossing roller to chill and solidify the film with an embossed pattern for reasons discussed further below. The precursor film is preferably produced to a gauge of 4 to 6 mils, which allows for further stretching as described below. The extrusion temperatures, die temperatures, and embossing roll temperatures will depend on the composition employed, but generally will be in the following ranges for compositions of the present invention prepared by cast extrusion:

	Melt Temperature (°F)	350-450
25	Die Temperature (°F)	350-450
	Embossing Roll Temperature (°F)	70-130

Film formation by tubular extrusion produces balanced films having increased film strength in both the machine and cross-machine direction. In the tubular blown film process, the film forming composition is first melted and then extruded through an annular die. The die should preferably have a die gap suitable for extruding LLDPE resin which normally is greater than about 0.5 mm and preferably greater than 0.75 mm. The film forming composition is extruded at a melt temperature between about 150°C to 300°C, preferably between 190°C and 240°C. The molten composition is preferably extruded in an upward

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elastomers, stabilizers against heat or ultraviolet rays, pigments, antistatic agents, etc. may be added to the compositions in the conventional manner. Variations in composition and manufacturing techniques will be readily apparent to persons skilled in the art of manufacturing polyolefin films and are within the scope of this invention. In the examples which follow water vapor transmission rates (WVTR) were measured in accordance with ASTM F372-73 using a Permatran W1 analyzer manufactured by Modern Controls International Inc.

Example 1 (COMPARISON)

A linear low density polyethylene which consisted of a copolymer of ethylene and hexene-1 was compounded with an equal weight of a surface treated calcium carbonate. The calcium carbonate was surface treated with calcium stearate to render the surface of the particles hydrophobic. The resulting formulation was cast extruded into a precursor film having a thickness of approximately 4 to 6 mil.

The resulting precursor film was cooled and then subjected to tentering stress in the transverse direction with a stretch ratio of 4 to 1 and a film speed of about 60 meters per minute. Stretching was performed in a tentering frame with heat applied only to the final zone of the tentering frame. The temperature of the film in the final zone was maintained at about 93°C. As a result of convection within the tentering frame, stretching of the film occurred at approximately 60°C. The film became white and breathable when stretched and retained those properties following the heat setting treatment. The final breathable film had a water vapor transmission rate of up to 5800 grams per square meter per day at 38°C.

Example 2

The LLDPE/calcium carbonate composition of Example 1 was cast extruded under the same conditions as Example 1. The precursor film was passed between a smooth roller and a diamond patterned embossing roller. The resulting film had a thickness of approximately 4 to 6 mil and a diamond

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CLAIMS:

1. Method of making a permeable film, comprising the steps of:
 - mixing a polyolefin with a filler;
 - extruding a precursor film from the polyolefin/filler mixture;
 - melt embossing the precursor film to impose therein a pattern of different film thicknesses; and
 - stretching the melt embossed precursor film to impart greater permeability in the areas of reduced thickness thereof in comparison to the areas of greater thickness.
2. Method according to claim 1, further comprising the step of heat setting the stretched film at a temperature above the stretching temperature and below the softening temperature of the stretched film.
3. Method according to claim 1 or claim 2 wherein the polyolefin is a copolymer of ethylene and a C₄-C₁₀ alpha-olefin.
4. Method according to any of the preceding claims wherein the filler is calcium carbonate surface treated with calcium stearate.
5. Method according to any of the preceding claims wherein the precursor film is melt embossed with a diamond pattern.
6. Method according to any of the preceding claims wherein the polyolefin/filler mixture contains between about 15 percent to about 35 percent filler by volume.
7. Permeable film produced by a method according to any of the preceding claims.
8. Permeable film comprising:
 - a polyolefin and a filler; and
 - a pattern of different film thicknesses having greater permeability in the areas of reduced thickness thereof in comparison to the areas of greater thickness.

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9. Film according to claim 8 wherein the polyolefin is a copolymer of ethylene and a C₄-C₁₀ alpha-olefin; the filler is calcium carbonate surface treated with calcium stearate; the pattern of different film thicknesses is a diamond pattern, and/or wherein the filler is present in an amount between about 15 percent to about 35 percent by volume of the total amount of the polyolefin and the filler.

10. Method of making a permeable film, comprising the steps of:

mixing a polyolefin with a filler;
cast extruding a precursor film of the polyolefin/
filler mixture onto at least one melt embossing roller to impose
therein a pattern of different film thicknesses; and
stretching the melt embossed precursor film in the
transverse direction to impact greater permeability in the areas of
reduced thickness thereof in comparison to the areas of greater
thickness.

11. Method according to claim 10 in which there is further
provided the step of heat setting the stretched film at a temperature
above the stretching temperature and below the softening temperature
of the stretched film; wherein the polyolefin is a copolymer of
ethylene and a C₄-C₁₀ alpha-olefin; wherein the filler is calcium
carbonate surface treated with calcium stearate; wherein the
precursor film is melt embossed with a diamond pattern; and/or
wherein the polyolefin/filler mixture contains between about 15
percent to about 35 percent filler by volume.

12. Film produced by a method according to claim 10 or 11.

retype

- 1a -

temperature below 70°C produces a porous film. Some of the resulting films were stated to be both vapor and liquid permeable, however, at least one film (Example 3) was stated to be permeable to air. ~~and to be considered under Article 54(3) EPC~~

EP-A-232 060 of earlier priority date describes the production of a gas-permeable porous film of polyolefin ~~e.g. mix in the LLDPE and a filler, extruding a film, embossing and stretching the LLDPE produced by stretching a film of a mixture of the polyolefin and inorganic filler, the film possessing a rugged pattern on the surface.~~ The pattern is produced by an embossing roller and may be applied before and/or after stretching of the film. The pattern may be e.g. a satin finish or in the form of lines. US-A-4,921,653 equivalent to the above defines the rugged pattern as having peaks and valleys with a depth therebetween of from 2 μ m to 3 mm. ~~EP-A-232 060 does not disclose the specific nature of the LLDPE other than the melt index.~~ The present invention provides a method of making a ~~claim 1...~~ breathable film comprising the steps of:

~~mixing a polyolefin with a filler,
extruding a film from the polyolefin/filler mixture, and
stretching the film,
characterised in that:
the said polyolefin is a linear low density polyethylene copolymer produced by polymerising ethylene with a C₄-10 alpha-olefin, and
during or after fabrication the film is embossed to impose therein a pattern of areas of different film thicknesses with greater vapor permeability in areas of reduced thickness in comparison to areas of greater thickness.~~

The film may be produced by tubular extrusion and embossed thereafter. Preferably a precursor film is cast extruded and embossed prior to stretching.

The invention is inclusive of breathable film obtainable by the method described above characterised by a pattern of areas of different film thicknesses with greater vapor permeability in areas of reduced thickness in comparison to areas of greater thickness and an overall water vapor transmission rate in excess of 5,800 g/m²/day.

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CLAIMS

1. Method of making a breathable film comprising the steps of:
mixing a ~~polyolefin~~^{precursor} with a filler,
extruding a ~~film~~^{precursor} from the polyolefin/filler mixture, and
stretching the film,
characterised in that:
the said ~~polyolefin~~^{precursor} is a linear low density polyethylene
copolymer produced by polymerising ethylene with a C₄-10
alpha-olefin, and
during or after fabrication the film is ~~embossed~~^{melt} to impose
therein a pattern of areas of different film thicknesses ^{and} with to impart
greater vapor permeability in areas of reduced thickness in
comparison to areas of greater thickness.
2. Method according to claim 1 wherein the filler is calcium
carbonate treated with calcium stearate.
3. Method according to claim 1 or claim 2 wherein the
polyolefin/filler mixture contains from 15 to 35 vol.% filler.
4. Method according to any preceding claim wherein said
alpha-olefin is selected from butene-1, pentene-1,
4-methylpentene-1, heptene-1 and octene.
5. Method according to any of claims 1 to 3 wherein said
alpha-olefin is hexene-1.
6. Method according to any preceding claim wherein said
alpha-olefin is present in amount from 3 to 14 wt.%.
7. Method according to any preceding claim wherein said LLPDE
copolymer has a density from 0.900 to 0.935 g/cm³.
8. Method according to any preceding claim wherein the
unstretched film has a thickness from 102 to 152 um (4 to 6
mil.)

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